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A COMPARATIVE STUDY OF THE FLUORESCENCE AND THE EMISSION SPECTRA OF ANISOLE

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Plate III

ABSTRACT. The fluorescence and emission spectra of anisole vapour have been photographed in the near ultraviolet region. The two spectra are compared and their vibrational structure has been discussed on the basis of 13 ground state frequencies observed in the fluorescence spectrum and 15 ground state and 7 excited state frequencies observed in the emission spectrum.

INTRODUCTION

The present paper deals with the investigation of the fluorescence and emission spectra of anisole vapour. A preliminary report on the fluorescence spectrum has already been published (Prakash, 1962) The fluorescence was excited by condensed manganese spark lines and it lies in the near ultraviolet region. The emission spectrum of the molecule first photographed by Singh (1958) in this laboratory was excited by transformer discharge. This spectrum also lies in the near ultraviolet region, but is more extended. Both the processess involve transitions from an excited electronic state to the various vibrational levels of the ground electronic state. A comparative study of the two spectra has provided better information about the vibrational structure of the states involved.

EXPERIMENTAL

Fluorescence spectrum

The fluorescence spectrum of anisole vapour has been recorded following the technique of Bass and Sponer (1950). The exciting source was a condensed manganese spark working at 15000 volts drawn from a Hilger 1/4 KW transformer with a condenser of capacity .05μF kept in the circuit parallel to the spark gap. A horn shaped fluorescence cell of pyrex glass fitted with three quartz windows was used. The liquid was obtained from E. Merck, Darmstadt and was of their extra pure quality. It was used as such without further purification. The liquid at room temperature was contained in a small bulb attached to a side tube of the fluorescence cell. The vapour pressure of the chemical was about 7 to

8 mm of mercury. The exciting radiation was focussed on the entrance window by a short focus quartz lens. A concave mirror with a wide aperture was used at the back of the spark source to increase the intensity of the exciting radiation.

The fluorescent radiation was received in a direction at right angles to the incident beam and was photographed on the Hilger medium quartz spectrograph having an aperture f/12 and dispersion of 13 Å/mm in the region around 2700 Å. The cell was placed very close to the slit of the spectrograph. The intensity of the fluorescent radiation was further increased by placing a plane mirror behind the cell and facing the slit of the spectrograph. Kodak II-0 plates were used and an exposure of 110 hours was found sufficient to record the spectrum with a slit width of 35 microns.

Emission spectrum

The emission spectrum of anisole has been obtained by uncondensed transformer discharge through flowing vapour. The usual π type discharge tube, 75 cm. long, fitted with internal aluminium electrodes was used. The tube was sealed off at one end and the other end was closed with a quartz window. A bulb, containing liquid anisole was attached to the discharge tube through a nail trap. This served to control the flow of vapour in the discharge tube. The tube was evacuated by means of a vacuum pump through a U-shaped glass tube kept immersed in ice and salt mixture to condense the vapour coming from the discharge tube. At a regulated flow of the vapour a light blue discharge was found to emit the bands. This type of discharge was maintained throughout the experiment by controlling the output of the transformer at about 3000 volts by means of a variac, put in the primary of the transformer.

The spectrum was photographed on Zeiss medium quartz spectrograph with slit width of 35 microns. Kodak II-0 plates were used to photograph the spectrum with different times of exposures varying from 1 to 4 hours.

RESULTS

Both the fluorescence and emission spectra reproduced in Fig. 1 seem to be alike and lie in the region 2700 Å to 3100 Å. The bands in the emission spectrum are sharper and more extended than those in the fluorescence spectrum. The bands in both the cases are red degraded and are masked by a strong continuum covering the entire region of the spectra. The intensities of the bands on the shorter wavelength side of the spectrum have been reduced due to self-absorption by the unexcited vapour lying near the window.

The bands were measured using Hilger L76 comparator with a least count of .001 mm. The wavenumbers are accurate up to ± 8 cm^{-1} for fluorescence bands and up to ± 5 cm^{-1} for emission bands.

The fluorescence and emission bands are collected in Table I, together with their wavenumbers, the intensities, the separations from 0, 0 band and their

assignments. The figures in parentheses give the difference in wave-numbers between the observed and assigned values. The notations used to indicate the intensities of the bands are as follows :-

vw–very weak, w–weak, mw–medium to weak, m–medium, ms–medium to strong, s–strong, vs–very strong, d–diffuse, b–broad.

In Table II, a comparison between the fundamental ground state frequencies observed in fluorescence, emission, absorption and Raman spectra is given.

DISCUSSION

If we take OCH_3 to behave like an atom X, the approximate symmetry of anisole is C_{2v}. Though this is not rigorously true, it serves our purpose to explain the gross structure of the spectrum. From the work of Sponer and Teller (1941) it can be concluded that the spectra of mono-substituted benzenes observed in the ultraviolet region corresponds to the electronic transition $^1B_1 \rightarrow {}^1A_1$, between the totally symmetric ground state (A_1) and a non-totally symmetric excited state (B_1). In an allowed transition, we expect strong 0, 0 band, which, however, in our case has appeared as a self-absorption band. We further expect strong totally symmetric vibrations (a_1) and weak non-totally symmetric vibrations (a_2 and b_1) to appear in our spectra. The non-totally symmetric vibrations (b_2) should occur with even quanta only and in combination with non-totally symmetric vibrations (a_2 and b_1).

The strong absorption band due to self-absorption at 36386 cm^{-1} in the fluorescence spectrum or at 36387 cm^{-1} in the emission spectrum is purely due to an electronic transition and is taken as the 0,0 band in the present analysis. This is in agreement with the value 36389 cm^{-1} measured in ultraviolet absorption (Sreeramamurty 1950) spectrum.

The analysis of the fluorescence bands shows the following ground state frequencies : 265, 450, 522, 555, 611, 788, 818, 1000, 1029, 1178, 1250, 1310 and 1597 cm^{-1}. A similar analysis of the emission bands shows all the above frequencies observed in the fluorescence spectrum with an addition of two frequencies, namely, 209 and 1065 cm^{-1}. Other frequencies are 265, 448, 520, 551, 615, 785, 820, 996, 1023, 1180, 1251, 1302 and 1599 cm^{-1}. These correspond well with values mentioned in the case of fluorescence.

The frequencies 788, 1000, 1029 and 1250 cm^{-1} in the fluorescence are correlated with 785, 996, 1023 and 1251 cm^{-1} in the emission spectrum. They are excited strongly and are observed in combination and overtones. This has led us to believe that they are totally symmetric vibrations. The corresponding Raman frequencies (Kohlrausch and Pongratz, 1934) are at 781, 991, 1020 and 1244 cm^{-1} respectively. The vibrations $\sim$785 and $\sim$ 1251 cm^{-1} in our spectra are X sensitive corresponding to the frequencies 785 and 1210 cm^{-1} observed in toluene (Pitzer and Scott, 1943). The frequency $\sim$996 is the strongest and

corresponds to breathing vibration. The vibration ~1023 cm^{-1} is due to C–H in-plane bending vibration. This is inferred by comparing with frequencies 1024, 1029 and 1030 cm^{-1} occurring in phenol (Evans 1960), aniline (Evans 1960) and toluene (Pitzer and Scott, 1943).

The vibrations 1178, 1310 and 1557 cm^{-1} observed in the fluorescence spectrum also occur in emission with the values 1180, 1302 and 1599 cm^{-1} respectively. The true intensities of the bands involving these vibrations cannot be visualized as the bands have been completely masked by the strong continuum predominating in that region. These can be correlated with frequencies 1177, 1299 and 1603 cm^{-1} in the Raman spectrum. The frequency 1180 can be assigned to C—H inplane bending vibration of type a_1 by analogy with the frequencies 1170, 1176 and 1178 occurring in phenol, aniline and toluene respectively. The remaining two vibrations lie in the region of C–C stretching vibrations, but the spectra do not give any definite information about their species.

A very weak frequency 1065 cm^{-1} has been recorded in emission spectrum. It finds the proper correlation with the frequency 1072 cm^{-1} in the Raman spectrum.

A medium to weak frequency 818 cm^{-1} in the fluorescence or 820 cm^{-1} in the emission spectrum is correlated with the frequency 816 cm^{-1} in the Raman spectrum. This frequency is expected to be a_2, C–H out-of-plane bending vibration, split out of 849 e_g^- vibration of benzene.

The weak frequency 611 cm^{-1} in the fluorescence or 614 cm^{-1} in the emission spectrum is the non-totally symmetric part of 606e_g^+ vibration of benzene. The corresponding part in the Raman spectrum is at 612 cm^{-1}.

A strong vibration 551 cm^{-1} occurs in the emission spectrum and is also found in combination with totally symmetric vibrations. This may be taken as a fundamental vibration, but no corresponding frequency in the Raman spectrum is reported. It occurs in fluorescence with weaker intensity.

The frequencies 520, 448, 265 and 209 cm^{-1} are observed with weaker intensities in the emission spectrum. They lie in the region of self-absorption and no definite information about their species could be gathered from the spectrum. They are correlated with frequencies 529, 441, 264 and 210 cm^{-1} in the Raman spectrum. In the fluorescence spectrum they are more uncertain. However, the two low vibrations 209 and 265 cm^{-1} may be assigned to bending modes.

The emission spectrum also extends towards shorter wavelength side of the 0, 0 band. The bands appear due to self-absorption and involve the excited state frequencies . 184, 252 495, 522, 759, 934 and 954 cm^{-1}.

The frequencies 30, 56 and 230 cm^{-1} observed in the fluorescence are in close agreement with the values 28, 58 and 230 cm^{-1} in the emission spectrum. They are assigned to difference frequencies arising out of 1-1 transitions of some

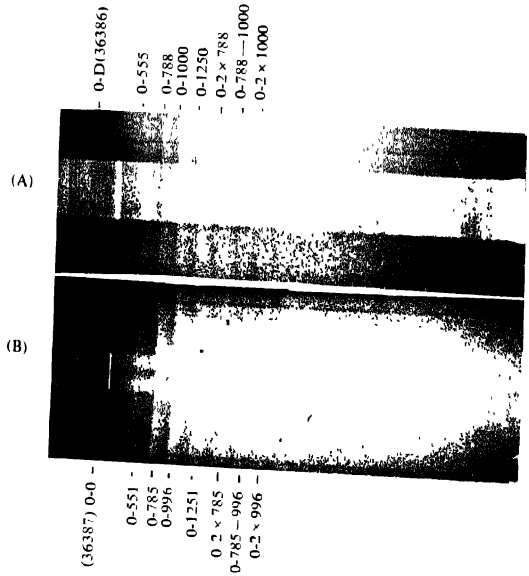

Fig. 1. (A) Fluorescene and (B) emission spectra of anisole vapour.

TABLE I

Fluorescence and emission bands of anisole

Fluorescence spectrum				Emission spectrum			
Wave-number	Intensity	Separation from 0,0	Assignment	Wave-number	Intensity	Separation from 0,0	Assignment
				37341	m	954	0+954 (0)
				37321	m	934	0+934 (0)
				37146	m	759	0+759 (0)
				37119	mw	732	0+759−28 (1)
				37087	w	700	0+759−58 (−1)
				36909	m	522	0+522 (0)
				36882	m	495	0+495 (0)
				36847	mw	460	0+522−58 (4)
				36812	vw	425	
				36752	mw	365	0+2×184 (3)
				36678	w	291	0+522−230 (−1)
				36639	w	252	0+252 (0)
36386	vs	0	0−0 (0)	36387	vs	0	0−0 (0)
36356	s	−30	0−30 (0)	36359	m	−28	0−28 (0)
				36351	w	−36	
36330	s	−56	0−56 (0)	36329	msb	−58	0−58 (0)
36299	w	−87	0−56−30 (−1)	36299	mwb	−88	0−58−28 (−2)
				36291	vw	96	0−614+522 (−4)
36266	w	−120	0−2×56 (−8)	36272	mw	−115	0−2×58 (1)
				36242	vw	145	
				36178	vw	−209	0−209 (0)
36153	mw	−233	0−230 (−3)	36158	m	−229	0−230 (1)
36121	vw	−265	0−265 (0)	36122	vw	−265	0−265 (0)
				35973	vw	−414	0−2×209 (4)
35936	vw	−450	0−450 (0)	35939	vw	−448	0−448 (0)
				35927	vw	−460	0−2×230 (0)
35864	vw	−522	0−522 (0)	35869	vw	−518	0−520 (2)
			0−2×230−56 (−6)				0−2×230−58 (0)
35831	mw	−555	0−555 (0)	35836	m	−551	0−551 (0)
				35812	vw	−575	0−551−28 (4)
35775	w	−611	0−611 (0)	35770	w	−617	0−614 (−3)
35752	vw	−634	0−611−30 (−3)				
35718	vw	−668	0−611−56 (−1)	35720	vw	−667	0−614−58 (5)
				35685	vw	−702	
				35648	vw	−739	
35598	ms	−788	0−788 (0)	35602	ms	−785	0−785 (0)
35568	mw	−818	0−818 (0)	35567	mw	−820	0−820 (0)
35542	w	−844	0−788−56 (0)	35546	w	−841	0−785−58 (2)

TABLE I (*contd*).

Fluorescence spectrum				Emission spectrum			
Wave-number	Intensity	Separation from 0,0	Assignment	Wave-number	Intensity	Separation from 0,0	Assignment
35506	w	−880	0−818−56 (−6)	35508	vw	−879	0−820−58 (−1)
35486	w	−900	0−788−2×56 (0)	35491	vw	−896	0−785−2×58 (5)
35418	vw	−968	0−522−450 (4)	35417	w	−970	0−448−520 (−2)
35400	vw	−986					
35386	ms	−1000	0−1000 (0)	35391	ms	−996	0−996 (0)
35357	m	−1029	0−1029 (0)	35364	m	−1023	0−1023 (0)
35330	mw	−1056	0−1000−56 (0)	35338	w	−1049	0−996−58 (5)
				35322	vw	−1065	0−1065 (0)
35306	mw	−1080	0−1029−56 (5)	35305	vw	−1082	0−1023−58 (−1)
35279	w	−1107	0−1000−2×56 (5)	35276	vw	−1111	0−996−2×58 (1)
35250	w	−1136	0−611−522 (−3)	35247	vw	−1140	0−1023−2×58 (−1)
35208	w	−1178	0−1178 (0)	35207	w	−1180	0−1180 (0)
35167	w	−1219	0−2×611 (3)	35162	w	−1225	0−2×614 (3)
35136	w	−1250	0−1250 (0)	35136	m	−1251	0−1251 (0)
35108	w	−1278	0−1250−30 (2)	35109	vw	−1278	0−1251−28 (1)
35076	vw	−1310	0−1310 (0)	35085	w	−1302	0−1302 (0)
				35050	vw	−1337	0−785−551 (−1)
35020	vw	−1366	0−1310−56 (0)				
				34844	vw	−1543	0−996−551 (4)
34816	w	−1570	0−2×788 (6)	34813	w	−1574	0−2×785 (−4)
34789	w	−1597	0−1597 (0)	34788	w	−1599	0−1599 (0)
34753	vw	−1633	0−2×788−56 (−1)	34757	vw	−1630	0−2×785−58 (−2)
				34742	vw	−1645	0−2×820 (−5)
34723	vw	−1663					
34597	wd	−1789	0−1000−788 (−1)	34606	mw	−1781	0−996−785 (0)
34568	vwd	−1818	0−1029−788 (−1)	34581	w	−1806	0−1023−785 (2)
				34558	vw	−1829	0−996−785−58 (10)
				34529	vw	−1858	0−1023−785−58 (8)
34385	vwd	−2001	0−2×1000 (−1)	34387	vwd	−2000	0−2×996 (8)
34366	vwd	−2020	0−1000−1029 (9)	34357	vwd	−2030	0−996−1023 (−11)

TABLE I (*contd*).

Fluorescence spectrum				Emission spectrum			
Wave-number	Intensity	Separation from 0,0	Assignment	Wave-number	Intensity	Separation from 0,0	Assignment
34332	vwd	−2054	0−2×1029 (4)	34335	vwd	−2052	0−2×1023 (6)
34300	vwd	−2086	0−1000−1029 −56(1)	34307	vwd	−2080	0−996−1023− 58 (−3)
	vwd	−2121		34264	vwd	−2123	
				34205	vwd	−2182	0−1180− 996 (−6)
				34146	vwd	−2241	0−996−1251 (6)
				34120	vwd	−2267	0−1023−1251 (7)
				34088	vwd	−2299	0−996−1251− 58 (6)
				34052	vwd	−2335	0−1023−1251− 58 (−3)
				34025	vwd	−2362	
				34001	vwd	−2386	
				33942	vwd	−2445	0−1251− 1180 (−14)
				33828	vwd	−2559	0−996−2× 785 (7)

TABLE II

Comparison between the fundamental ground state vibrations of anisole

Raman Kohlrausch and Pongratz	Fluorescence (Present Research)	Emission (Present Research)	Absorption Sreeramamurty	Assignment
210	—	209	210	b_2 nontotally symmetric
264	265	265	264	nontotally symmetric
441	450	448	440	—
529	522	520	523	—
—	555	551	—	a_1
612	611	614	610	b_1 ring def. ip
781	788	785	786	a_1 X sensitive stretch.
816	818	820	818	a_1 C-H bend. op
991	1000	996	987	a_1 ring breathing
1020	1029	1023	1029	a_1 C-H bend. ip
1072	—	1065	1055	b_1 C-H bend. ip
1177	1178	1180	—	a_1 C-H bend. ip
1244	1250	1251	—	a_1 X sensitive stretch.
1299	1310	1302	—	—
1603	1597	1599	—	ring stretch.

ip—inplane op—out of plane

suitable non-totally symmetric vibrations. The difference frequency 28 cm^{-1} may be explained as $0-210+184\ cm^{-1}$. No definite assignments could be given for the other two difference frequencies.

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